A DIALDEHYDE STARCH PRETANNAGE FOR RAPID TANNING OF SOLE LEATHER*

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ABSTRACT

A sole leather tannage is described consisting of a pretannage with dialdehyde starch followed by a rapid vegetable tannage in strong liquors. Chemical and physical data on the finished leather indicate that it is quite similar to commercial sole leather.

INTRODUCTION

The current tanning of heavy leather with vegetable tannins is a relatively long process. Although the time of tannage has been shortened somewhat by greater chemical control and mechanical improvements, several weeks are still required. A rapid and economical method of tanning would be of advantage to the industry.

Attempts have been made to shorten the time by the use of strong liquors, mechanical action, pH control, and control of the acid and salts content as described by Kay (1). The use of stronger liquors and mechanical action, such as drumming, accelerates the tanning process but has a tendency to damage the leather, usually causing "pebbling of the grain". It has been found that if leathers are given a pretannage with various inorganic or organic materials (chromium, syntans, etc.), this pebbling effect may be minimized. One of the materials that has been used in this manner is formaldehyde. The principles of the aldehyde tannage are described by Mellon (2), who also gives a complete bibliography.

There are only a few references to the pretannage of vegetable-tanned leather with formaldehyde, although numerous tannery experiments have been run. It has been found that this pretannage protects the leather from drawn grain in subsequent drumming and, in addition, accelerates the rate of penetration of tannin into the hide. The resulting leather is predominantly of the vegetable-tanned type, showing little effect of the formaldehyde pretannage (3, 4). This pretannage, although successful in accelerating vege-

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table tannage, has serious disadvantages, so that it is seldom used. Formaldehyde is unpleasant and somewhat dangerous to work with, and the finished leather has a tendency to be hard, flat, tinny, and cracky.

Within the last few years other types of aldehydes have been found to have tanning properties. Some of the dialdehydes are of particular interest. Seligsberger, Mann, and Clayton (5, 6) have recently reported on the use of glyoxal as a pretannage for a lignosulfonate tannage. These authors also give data obtained with other aldehydes, including dialdehyde starch supplied by this Laboratory. A preliminary report from this Laboratory on the tanning power of dialdehyde starch has been presented (7). Dialdehyde starch is a polyfunctional aldehyde derived from starch by periodate oxidation (8, 9, 10). These investigations indicated that this material might have advantages over formaldehyde as a pretanning agent. Preliminary tests on small pieces of hide in battery jars were promising and were continued on a larger laboratory scale. The latter will be discussed in this paper.

In these tests we have not attempted to produce a new type of leather but to produce an established type of leather by a shorter process.

EXPERIMENTAL

Outline of Procedure

A. Hide Preparation

1. Unhaired by conventional lime-sulfide
2. Washed for ½ hr. in drum with running water or for 2 hr. in a still vat
3. Adjustment of pH
   a. In pH 4.5 buffer overnight; or
   b. Drum for 4 hr. with 2% ammonium chloride (pH 8.5–9.0) 0.1% Oropon N*

B. Pretanning with Dialdehyde Starch

1. Tanning liquor:
   Sodium sulfate—8% (solution basis)
   Sodium bicarbonate—6.3% (white-weight basis)
   Water—300 to 500% (white-weight basis)
   Dialdehyde starch—5, 10, or 15% (white-weight basis)
2. Tanning conditions
   a. In drum—7 to 16 hr.
   b. In still vat—1 to 2 days

*The mention of trade names or companies throughout this paper does not constitute an endorsement by the Department of Agriculture over other products of a similar nature not mentioned.

C. Vegetable Retannage

1. Tanning liquor
   a. Blend of quebracho and chestnut extracts
   b. Tannin concentration—14 to 15%
   c. pH—3.8 to 4.2
2. Tanning conditions
   a. In drum—8 hr. drumming and 16 hr. standing
   b. In still vat—4 to 5 days

D. Finishing

The leather was wheel-extracted, bleached, oiled, loaded, and rolled in the conventional manner.

Details of Procedure.—For each test one side of a hide which had been unhaired in the laboratory by a lime-sulfide process was cut into bend, belly, and shoulder. These were washed in a drum for ½ hr. with running water or left in still water for 4 hr. After the washing they were brought to the desired pH. Preliminary tests had shown that this pH could vary over a range of 4.5 to 9.0 with apparently satisfactory results in dialdehyde starch tannage. A tannage at approximately pH 4.8, near the lower level, and one at approximately 8.5, near the upper level, were selected for these tests.

To bring the hides to pH 4.8 they were treated by immersion for at least 24 hr. in a solution of 10% sodium chloride, 3.5% sodium acetate, and 1.8% glacial acetic acid, using a solution-to-hide ratio of 3 to 1. For the pH level of 8.5 the hide pieces were drummed slowly for 4 hr. in a solution of 2% ammonium chloride and 0.1% Oropon N (on the white-hide weight) with a ratio of 3 to 1. The interior of the hide was then about pH 8.5 and the surface about 8.0. After the pH was adjusted, the hide pieces were washed with running water in the drum for ½ hr.

The hides were pretanned by suspending in a 300–500% volume of an 8% sodium sulfate solution containing 6.3% sodium bicarbonate and either 5, 10, or 15% dialdehyde starch (on the white-hide weight). This was preferably made up as a stock solution several times this strength. The calculated amounts of sodium sulfate and sodium bicarbonate were added to the water which was only slightly above room temperature. After these were dissolved by stirring, the dialdehyde starch was added in several portions. After a further stirring of about ½ hr. the dialdehyde starch was partially dissolved, the balance being in a highly dispersed suspension. When diluted for use the pH ranged from 7.8 to 8.4.

The dialdehyde starch pretannage was conducted either in a drum or in a still vat. The wooden drum used was 56″ in diameter and 26″ wide. It was

equipped with a variable speed drive to operate between 2 and 20 rpm. The hide pieces were drummed intermittently for 7 hr. at the lowest speed. If at this time the shrinkage temperature was 75°–80°C., and there was only a slight, dark, shrunken streak in the center of the hide, it was considered ready for vegetable tanning. If these conditions were not met, the leather was left overnight without motion.

In the still vat pretannage the pieces were suspended in a copper-lined vat with a liquor-to-hide ratio of 5 to 1. Penetration in this vat required 24 to 48 hours. The proper duration was determined as before by shrinkage temperature measurements.

The pieces of hide pretanned by either of the above methods were washed in running water for ½ hr. prior to entering the vegetable tanning liquor. The vegetable retannage was carried out in either a drum or in a still vat. The tanning liquor was made up to contain 14 to 15% tannin from a blend of 50% clarified quebracho extract and 50% imported chestnut extract (on a tannin basis). The liquor was used for a total of 20 times with appropriate strengthenings to maintain the tannin content. The pH was maintained at approximately 4.0. After each test the liquor was settled, and about 10% of the volume (equal to 7 to 8% of the original tannin content) was discarded before strengthening for the next test. The dialdehyde starch liquors were made fresh for each tannage. Penetration was rapid in the drum, being complete either in 8 hr. drumming or by this drumming followed by standing 16 hr. In the still vats penetration required 3 to 5 days. In each case the leather was washed for 10 to 15 min. and was then ready for extracting and finishing.

Some of the leathers were extracted, bleached, oiled, and finished at a commercial tannery. When returned to the laboratory the leathers were analyzed and tested for physical properties by the Official Methods of the American Leather Chemists Association (11) where possible.

RESULTS

The variables involved in these tests will be considered first as to their immediate effects, and secondly as to their apparent effects upon the finished leather. No immediate effects were noted by the variation in the pH values of the hides before tanning. As judged by shrinkage temperature determinations, each pH tested gave good penetration and fixation of the dialdehyde starch. The variations in the amounts of dialdehyde starch used resulted in changes in penetration and fixation of the dialdehyde in proportion to the amount used.

A comparison of drum tanning with vat tanning shows that penetration and fixation of the dialdehyde starch are much more rapid in the drum. However, in our tests, drum tanning caused a raised grain and pebbling. For the vegetable tannage, drum tanning is again much more rapid than vat

tanning with little danger of pebbling, except for a moderate amount on hides pretanned with only 5% dialdehyde starch.

The vegetable tanning liquors were kept at approximately the same tannin content and pH. The barkometer increased gradually and the purity decreased with the reuse of the liquors. These variations had little measurable effect on the rate of penetration or fixation of the tannin.

Table I shows the analyses of the vegetable tanning liquors; Table II shows the uptake of tannin from some of these liquors.

TABLE I

ANALYSES OF VEGETABLE LIQUOR USED FOR RETANNAGE OF DIALDEHYDE STARCH–PRETANNED HIDES

Expt. No.*	Barkometer Degrees	Total Solids %	Soluble Solids %	Tannin %	Purity Tan/SS × 100	pH
1	75	18.7	18.5	14.7	79.5	3.7
2	78	18.2	18.0	13.9	77.2	3.8
3	78	18.6	18.5	13.9	75.5	3.9
4	78	18.5	18.3	13.7	74.5	4.0
5	81	19.3	19.1	14.2	74.7	4.1
6	88	21.2	20.9	15.7	75.4	3.7
7	75	18.5	18.2	14.0	76.5	3.9
8	81	19.4	19.1	13.9	72.7	4.7
9	93	22.0	21.6	14.9	68.9	4.2
10	90	21.1	20.6	13.7	66.2	4.2
11	94	22.0	21.7	14.1	65.1	—
12	95	21.9	21.7	13.8	63.6	4.2
13	100	23.1	22.7	14.8	65.1	4.2
14	102	23.4	23.2	15.1	65.1	4.2
15	104	23.3	22.9	14.2	62.1	4.1
16	104	23.7	23.3	14.6	62.7	4.1
17	109	25.1	24.8	16.1	65.0	4.1
18	105	23.8	23.4	14.9	63.6	4.2
19	105	23.9	23.4	14.3	60.9	4.1
20	103	23.5	23.2	14.3	61.6	4.2
21	108	24.4	24.1	14.9	61.8	4.2

*Sampled immediately before each use.

All the leathers had a good color and general appearance, being well-filled and moderately flexible, and showing no tendency for the grain to crack.

Some typical analyses of the leathers are shown in Table III. These indicate that the variations in tanning methods have had little effect upon the final analytical values. They also indicate that these leathers are comparable analytically with sole leather of current production.

TABLE II

UPTAKE OF TANNIN FROM VEGETABLE LIQUORS
BY DIALDEHYDE STARCH–PRETANNED HIDES

Expt. No.	Sappage of Tannin from Liquor %	Weight of Liquor g.	Sappage of Tannin g.	White Hide Weight g.	Uptake of Tannin/100g. White Hide g.
2	5.57	80,000	2,856	9,600	29.8
3	4.16	54,000	2,246	9,092	24.7
4	3.66	54,000	1,976	9,675	20.4
5	4.52	54,000	2,441	9,532	25.6
6	3.72	56,000	2,083	8,990	23.2
7	5.33	80,000	4,264	20,600	20.7
8	4.57	80,000	3,656	17,200	21.3
9	3.95	80,000	3,160	19,600	16.2
10	3.51	80,000	2,808	18,000	15.6
11	5.21	80,000	4,168	16,800	24.8
14	4.93	80,000	3,944	19,600	20.1
15	5.15	80,000	4,120	19,170	21.5
16	3.56	80,000	2,840	16,200	17.6
17	3.17	80,000	2,536	15,925	15.9
18	3.15	80,000	2,520	16,570	15.2
19	3.23	80,000	2,580	14,800	17.5
20	3.18	80,000	2,540	14,900	17.0
21	3.18	80,000	2,128	13,500	15.9
				Average	20.2
				Standard Deviation ±	4.2

Table IV gives the results of physical tests upon the finished leathers—tensile strength, elongation, grain crackiness, piping, compressibility, rate of abrasion, and water absorption. For comparison, data from comparable leathers from three commercial tanneries are also given. In all cases the values are quite comparable, and all conform easily to federal specifications.

DISCUSSION

An interesting property of the dialdehyde starch pretannage step is the variation permissible in the condition of the hide before entering the tanning liquor. In most tannages it is necessary to condition the hide to retard fixation of the tanning material until penetration is accomplished. This is not necessary with the dialdehyde starch pretannage. A simple deliming process with ammonium chloride and a light bating are sufficient.

For the pretannage apparently 5% dialdehyde starch is sufficient. The properties of the finished leather are predominantly those of a vegetable-tanned leather, and the purpose of the dialdehyde starch pretannage is

TABLE III

ANALYSES* OF DIALDEHYDE STARCH–PRETANNED VEGETABLE SOLE LEATHERS (BENDS)

			Expt. 19	Expt. 16		Expt. 3		Expt. 6
State of tannage	Rough†	Finished	Finished	Finished	Finished	Finished	Finished	Finished
Method of pretannage	Vat	Drum	Vat	Vat	Vat	Drum	Vat	Drum
Method of vegetable tannage	Drum	Drum	Vat	Vat	Vat	Drum	Drum	Drum
Method of deliming	Buffer	Buffer	NH_4Cl	NH_4Cl	Buffer	Buffer	Buffer	Buffer
Dialdehyde starch used, %	15	5	5	10	15	15	15	20
Moisture, %	8.8	9.8	8.3	8.8	11.7	12.0	9.8	12.2
Petroleum ether extract,%	3.6	7.4	8.5	6.9	8.9	6.7	4.2	5.8
Insoluble ash, %	0.2	0.3	0.2	0.2	0.1	0.1	0.5	0.1
Hide substance,%	44.6	33.7	34.2	35.9	33.1	33.1	36.8	33.2
Soluble matter, %	10.8	25.5	26.2	24.2	21.1	22.0	24.1	21.7
Combined tannin, %	32.0	23.3	22.6	24.0	25.1	26.1	24.6	27.0
	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Degree of tannage	72.3	68.9	66.0	66.8	76.0	78.9	67.0	81.4
Soluble nontannin, %	2.6	17.8	17.5	16.4	12.7	13.9	17.0	13.0
Uncombined tannin, %	8.2	7.7	8.7	7.8	8.4	8.1	7.1	8.7
Total ash, %	0.2	5.8	5.5	5.2	3.9	4.3	5.4	4.0
pH value	——	3.7	3.7	3.8	3.8	3.8	3.2	3.9
Gain—white weight to finish, %	48.3	67.3	72.0	73.1	70.2	72.2	——	75.0

*All analyses calculated on the "as received" basis.
†After tanning at laboratory and before finishing.

TABLE IV

PHYSICAL PROPERTIES OF DIALDEHYDE STARCH–PRETANNED VEGETABLE SOLE LEATHER COMPARED WITH COMMERCIAL PRODUCTION

Bend No.	Tensile Strength[a] Thickness in.	Tensile Strength lb./in.^{2}	Elongation at[b] Break %	Elongation at[b] 200 lb. Load %	Grain Cracking[c] Mandrel Diameter[h] 16ths of an Inch A[k]	Grain Cracking[c] Mandrel Diameter[h] 16ths of an Inch B[k]	Piping[d] Mandrel Diameter[i] 16ths of an Inch	Compressibility[e] %	Abrasion[f] Loss in Weight, grams[j] Range	Abrasion[f] Loss in Weight, grams[j] Average	Water Absorption[g] Water absorbed after ½ hr. %	Water Absorption[g] Water absorbed after 2 hr. %	Water Absorption[g] Water absorbed after 24 hr. %
Dialdehyde Starch Pretanned–Vegetable Sole Leathers													
1	0.217	3,280	24	21	10	10	3	11.3	1.00–1.16	1.06	26.8	42.3	56.2
2	0.189	3,840	25	22	6	5	3	14.6	0.97–1.44	1.13	29.6	45.4	58.2
3	0.214	3,390	25	22	8	7	3	13.3	1.28–1.51	1.39	23.4	40.6	52.2
4	0.214	3,060	22	21	8	7	4	10.4	1.19–1.51	1.45	23.0	38.9	49.0
5	0.210	3,400	23	21	10	8	10	10.5	1.09–1.27	1.16	20.4	32.7	42.7
Average								12.0		1.24	24.6	40.0	51.7
Commercial Vegetable Sole Leathers													
1	0.239	3,320	17	15	12	10	14	9.7	1.13–1.49	1.30	27.0	48.9	61.0
2	0.213	3,780	27	17	8	8	16	8.2	0.95–1.64	1.41	21.2	32.5	45.7
3	0.214	3,390	24	20	8	8	14	13.2	1.46–1.74	1.55	21.9	41.9	54.1
4	0.200	3,150	25	21	10	8	12	12.0	0.96–1.42	1.20	26.6	43.1	56.7
Average								10.8		1.36	24.2	41.6	54.4

[a] ALCA Method E15. Test strips were 1 cm. wide. Each value is the average of 10 determinations.
[b] ALCA Method E17. Test strips were 1 cm. wide. Each value is the average of 10 determinations.
[c] ALCA Method E41 with modified mandrels. Samples ranged between 5.0 and 6.0 mm.
[d] ALCA Method E40 with modified mandrels. Samples ranged between 5.0 and 6.3 mm.
[e] ALCA Method E45. $\text{Compressibility} = \frac{\text{original thickness—compressed thickness}}{\text{original thickness}} \times 100$
[f] Measured on a cylinder 8″ in diameter covered with standard abrasive cloth and rotating at 100 rph. Leather pieces held against cloth by a weight of 250 g.
[g] ALCA Method E30. Reported as percentage of initial weight.
[h] Maximum diameter at which grain cracking was observed.
[i] Maximum diameter at which piping was observed.
[j] Grams of leather abraded from a 1-inch square by 400 revolutions of abrading cylinder. Ten samples were tested from each bend.
[k] Two samples taken from each leather adjacent to "A" sampling position.

merely to accelerate the rate of vegetable tanning. Therefore, a high level of dialdehyde starch pretannage is not necessary.

It would be advantageous to reuse the dialdehyde starch liquors by restrengthening, thereby saving some of the dialdehyde and all the other chemicals used. Preliminary tests indicate that the liquors may be restrengthened by adding 4% of dialdehyde starch and used in this manner for at least five times. Further confirmation is necessary.

The results indicate that the complete tannage could be carried out in rocker vats with limited motion. If drums or paddles are available, the time may be considerably reduced. In this case care must be taken to avoid pebbling during the pretannage with dialdehyde starch.

One of the difficulties of rapid tanning with strong vegetable liquors has always been the disposal of the liquors after tanning. For economical reasons it is necessary to reuse this liquor, but by continued reuse it loses its tanning power. The results indicate that the liquors used in this tannage reached an equilibrium and were still suitable for tanning with the loss of no more tannin than is lost in the tail liquors of conventional tannages.

The analytical results obtained on these leathers compare very favorably with those of commercially tanned sole leather. Since the tannage gives leather which is somewhat more flexible than normal, it should be capable of producing a highly flexible leather, if desired. Some yield may have to be sacrificed, as usually occurs in making flexible leather. The physical tests are of interest mainly in showing that the leathers are normal. There was no evidence of the stiffness, flatness, or crackiness usually associated with aldehyde-pretanned leathers. The water absorption property is normal, showing that the high rate of absorption of leather tanned with dialdehyde starch alone is not carried over into the vegetable tannage. The rate of abrasion appears satisfactory, although this measurement suffers from the defect common to all such measurements in that it is measured at only one abrasive force, whereas leather in practice is subjected to a variety of abrasive forces.

The economic feasibility of this process will depend upon balancing the cost of the extra material against the time saved. It will also depend upon the adaptation of the process to tannery equipment. To determine these points a large-scale tannery test is planned.

SUMMARY

It has been shown that a pretannage of heavy hides with a minimum of 5% dialdehyde starch on the white weight permits a rapid vegetable retannage using strong liquors.

The results indicate that regular tannery equipment may be used. Rocker vats appear to give suitable results for both the pretannage and the vegetable retannage. For a more rapid tannage, drums or paddles may be used, taking

precautions to avoid pebbling in the early stages of the dialdehyde starch pretannage.

The tests indicate that the vegetable tanning liquors may be reused repeatedly after discarding about 10% of the sap liquor, strengthening with fresh extract, and adjusting the pH to the proper level. At the point of equilibrium, the purity, penetration, and fixation of tannin are still satisfactory. The complete tannage requires a maximum time of seven days.

The data indicate that this leather is comparable with standard vegetable-tanned sole leather.

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DISCUSSION

J. F. WAGONER (Armour Leather Company): Mrs. Happich is to be congratulated on a very fine presentation. The data which she has presented reflect the quality of the work which we have learned to associate with the group at Eastern Regional Laboratory. The prime objective of this work has been to determine if leather comparable to commercial sole leather can be produced in a shorter period of time. Therefore, it is of particular interest,

as we are always endeavoring to effect a reduction in the time required for making sole leather.

In recent years the possibility of using the aldehydes as pretanning agents has come in for considerable study. The possible use of dialdehyde starch in this connection certainly merits our serious consideration. And I believe it is of particular interest at this time inasmuch as we are dealing with a comparatively new product which is only now beginning to approach production-scale levels.

The chemical analyses and the physical test data developed on these leathers, which have been produced on a laboratory-scale basis, seem to indicate that there is a good possibility of producing sole leather which compares very favorably with present-day sole leather. The work described provides a good foundation on which to proceed on the larger-scale testing that is necessary to evaluate the process fully from a technical and economic standpoint.

In examining the data it is interesting to note that with the reuse of the vegetable tanning liquor, there was an apparent decrease in tannin consumption, and yet the yields of leather based on the white weight are approximately the same.

I would like to ask Mrs. Happich for her views on this and also if she has any indication that there would be any marked decrease in the amount of vegetable tannins required to accomplish this tannage.

MRS. HAPPICH: The pickup of tannin as recorded was the pickup of tannin from our liquors. These leathers were extracted and finished in a commercial tannery afterward, where the yields became approximately the same. There was considerable tannin pickup by the leather during extracting.

MR. WAGONER: And do you feel that the data indicate that there would be a marked decrease in the amount of the vegetable tannins with dialdehyde pretannage?

MRS. HAPPICH: We do not have enough data to come to any conclusions on that at this time.

DR. LUDWIG SELIGSBERGER (U. S. Quartermaster Research and Engineering Center): Was the temperature in the drum measured? And if the drumming was continued for seven hours in the drum tannage, was the dialdehyde starch stable when the drum was heating up to maybe 90° to 95°F., or did losses occur?

MRS. HAPPICH: We were tanning only one side to a moderate-size drum, Dr. Seligsberger, and the increase in temperature was not very great.

DR. SELIGSBERGER: You don't think the drawn grain came from the action of the drum itself, without temperature increase?

MRS. HAPPICH: Yes, we think from the mechanical action.

DR. SELIGSBERGER: You would probably not need seven hours continuous drumming; I found with other aldehydes that it is not necessary to drum so much.

MRS. HAPPICH: That could be true. We drummed intermittently, also.

JOHN H. DAVIS (Marathon Corporation): I am interested in reuse or restrengthening of the vat liquors. You restrengthened and used them 20 times. What happens to that liquor after it has been used that length of time? Do you throw it away and start all over?

MRS. HAPPICH: We ended our experiment there; however, these liquors had apparently come to equilibrium, and we could have continued to use them. We think that there is a possibility that the discarded liquor could be used in making up the extracting liquor.